The University of Chicago.
FOUNDED BY JOHN D. ROCKEFELLER.

Thickness of the Black Spot on Liquid Films.

A DISSERTATION PRESENTED TO THE FACULTY OF ARTS, LITERATURE, AND SCIENCE OF THE UNIVERSITY OF CHICAGO, IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

DEPARTMENT OF PHYSICS.

By EDWIN SHELDON JOHONNOTT, Jr.

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By EDWIN S. JOHONNOTT, Jun.*

INTRODUCTION.

THE principal object of the measurement of the thickness of the black spot on certain liquid films is to determine the radius of molecular attraction, which is supposed to be equal to half the thickness of the film. The first determination of the thickness of the film was made by Plateau †, who gives it as 120×10^{-6} millim. or 120 $\mu\mu$. The present generally accepted value is that given by the experiments of Professors Reinold and Rücker ‡, viz., 12 $\mu\mu$ for the thickness.

They employed two methods, the first consisting in measuring the electrical resistance of cylindrical films, and the second in determining the relative retardation of two beams of light, one of which had been transmitted through a larger number of films than the other.

P. Drude §, by considering the effect of capillarity on the reflexion and refraction of light, obtained a value of 17 $\mu\mu$ for the thickness. He also gives a good historical summary of the work that has been done on the determination of the radius of molecular attraction. Lord Rayleigh ‖ has also shown that an olive-oil film 2 $\mu\mu$ thick will just quiet the movements of camphor particles on a water surface.

* Communicated by the Author.
† *Statique des Liquides*, vol. i. p. 210.
‡ Phil. Trans. 1881, p. 447; 1883, p. 645; and 1893 (A), p. 505.
§ Wied. *Ann.* vol. xliii. (1891), pp. 126–157 and 158–176.
‖ Proc. Roy. Soc. vol. xlvii. (1889–90), p. 364.

Two methods, both suggested by Prof. Michelson, were used in making the measurements here given,

the first, an interferometer method,

the second, a photometric method.

In the first method continuous readings, for the mean thickness of a number of films, were made over a period of several hours. In the second method the thickness of a single film was determined from the intensity of the light reflected at a series of different angles of incidence. Since it was impossible to obtain monochromatic lights sufficiently intense, this method does not furnish accurate results.

The liquid used was a solution of either oleate of soda or oleate of potash in distilled water, the proportions ranging from 1 part of oleate to 100 of water (1 : 100), to 1 part of oleate to 40 of water (1 : 40). Tests were made with potassium nitrate and also glycerine added to the above solutions.

The index of refraction of all the solutions was assumed to be that of pure water, viz., 1·333. All the measurements were made on vertical films, formed on rectangular frames made of glass fibre. The lower edge of the films was on the surface of the solution in all cases.

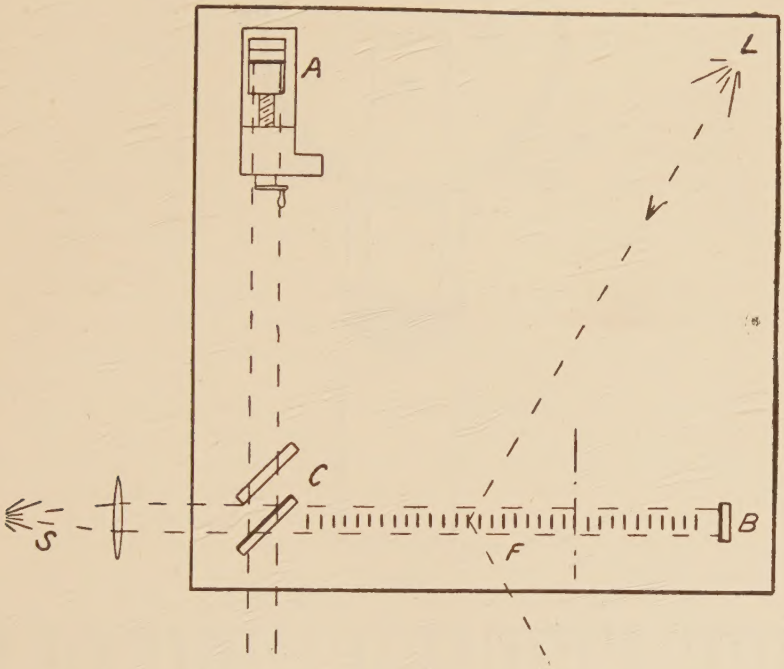
Method I.

Prof. Michelson's interferometer was used in making the measurements by this method.

Description of Apparatus.—The two reflectors were placed at A and B, on a stone slab 2 feet by 2 feet (fig. 1), and the separating surface and compensator at C. The films were brought into the path, BC, of the interferometer, at F, on frames made of glass fibre 0·5 millim. in diameter. In mounting the frames, a $\frac{3}{8}$-inch round brass rod 35 centim. long was slit lengthwise into halves. 60 grooves, at intervals of 5 millim. were ruled on the flat surface of one of the halves. A glass fibre 7 centim. long was clamped centrally in each groove by means of a long square rod faced with chamois skin. Upon levelling the plane of the fibres and carrying a fine flame along the edges of the grooved surface, all of the frames were formed in vertical planes. The frames were then all brought to a common length by forming beads on the lower ends with the flame. These ends were then lowered into molten solder in a trough made from a piece of $\frac{1}{2}$-inch brass tubing, slitted longitudinally. After cooling, the clamp was removed, leaving 54 frames rigidly mounted and perfectly in line at the tops and sides. Each end of the supports of the frames was then attached, by means of small wind-

lasses, to the ends of a zinc trough holding 500 cub. centim. of the solution. This was covered with a glass casing, C (fig. 2), made from a tube by removing a longitudinal section. Two optically plane parallel pieces of glass covered the ends of the case ; while two plane parallels of the same thickness

Fig. 1.



were placed at the ends of a similar piece of tubing in the other path of the interferometer. Cementing with beeswax or paraffin prevented any unsteadiness of the fringes, and also provided a practically air-tight chamber for the films.

Fig. 2 shows a full-sized cross-sectional view of the film box. The frames are shown anchored in the solder at D, while the film is shown formed at H. The temperature readings were taken with a thermometer, T, inside of the case, and held away from the walls by rubber rings.

Methods of Observation.—By turning the windlasses, the films could be brought into the path of the interferometer and so adjusted that the displaced fringes appeared contiguous with those from the light not going through the films. Using

Fig. 2.

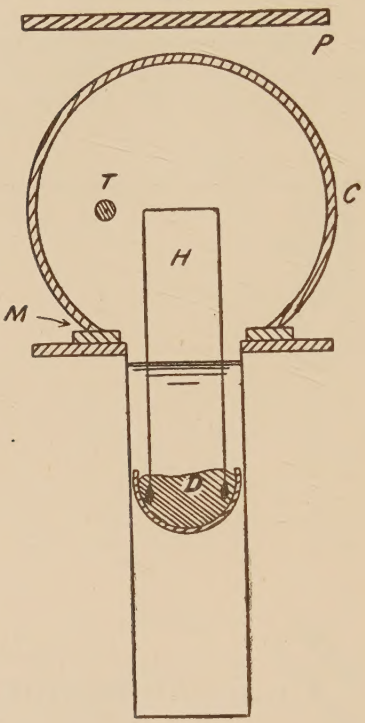
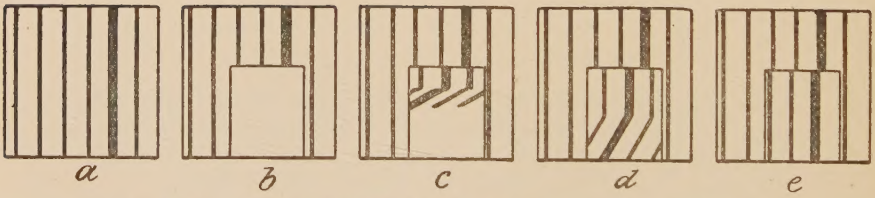


Fig. 3.



vertical fringes of white light, the appearance is as shown in fig. 3. (*a*) represents the appearance when the frames are below the surface of the solution ; (*b*) when the films are first formed. The fringes, of course, do not show within the image of the frames, and only the broad horizontal bands of the coloured films are seen. As soon as the black film forms at the tops of all the frames the vertical fringes are seen displaced within the frames, and take successively the appearances shown in (*c*), (*d*), and (*e*).

The number of fringes displacement is determined by that of the central black fringe in the white-light fringes, which is shown in the figures broader than the adjacent coloured fringes. The fringes continue vertical within the image of the frames until they reach the boundary between the black and coloured films, and then slant off at a continuously increasing slope as the black films extend lower. When the black films cover the field, which usually occurs within five minutes after the frames are raised, the appearance is shown in (*e*).

When the atmosphere about the films has been enclosed a day or more, the tops of the coloured films may occur on the same level, preventing at first the appearance of the sloping portion of the fringes. This would indicate a considerable discontinuity in the thickness at the junction of the black and coloured films. A bodily shift of the sloping portion (*c*) was often noticed.

Methods of Measurement.—One of the advantages of this method is that there can be no great difference in the optical path inside and outside of the frames at their tops, except that due to the films ; and the fact that the fringes usually continue vertical within the image of the frames indicates that there is practically none. Another advantage is that the deflexion is the same as that which would be due to a single transmission through twice the number of films.

The measurements were all taken at the tops of the frames when the fringes were vertical. The calculations were made by using the wave-length of sodium light in the formula, although the white-light fringes were as often used in taking the readings, which were always eye-estimates of the displacement of the fringes.

The equation

$$D = \frac{\delta\lambda}{2N(\mu-1)}$$

gives the relation for finding the mean thickness of the films where

δ is the observed displacement of the fringes,
N the number of films,
$\lambda = 589\,\mu\mu$, the wave-length of sodium light,
$\mu = 1{\cdot}333$, the index of refraction of pure water, and
D the mean thickness of the films.

The Two Black Films.—With all solutions a very rapid fall in the thickness occurs when the black films have just been formed, and continues with greater or less rapidity according as the atmosphere about the films is more or less

exposed to heat or to the atmosphere of the room. (The films will be said to be "exposed" when the casing is unsealed and the atmosphere about the films is exposed to that of the room at crevices along the casing M (fig. 2).) Solutions of oleate of soda or potash, without any salt or glycerine added, show the greatest and most sudden changes in thickness. It was observed that these sudden changes were always accompanied by the formation of a second black film within the first. When the case was open or only partially sealed, this second black was seen to form first on the more exposed films in the case, and on the side of the frames toward a distant source of heat. A group of round spots would appear, at least two millimetres from the frames, and would expand and multiply until the whole upper part of the films was covered with the second black. This was also the case with films tightly sealed if the casing was warmed with a flame. With exposed or heated films the second black would soon appear on all the frames, after it had formed on the most exposed. Many times it would form by the expansion of a single spot, appearing as though the spot were a region of slightly smaller surface-tension in the first black film.

The slightest occurrence of the second black film was distinctly seen by arranging a gas-jet at L (fig. 1), and observing the reflected light. The spots would occur first on the upper corner nearest the light, unless the side of the case opposite the light was unsealed, while that toward it was sealed ; then they would form first on the more exposed side. Oftentimes a thick silvery film would form on the frames, as a boundary to the second black film.

This could usually be produced by warming an exposed film.

The second black on a liquid film was first observed by Newton*. Reinold and Rücker† on one occasion succeeded in getting the two black films successively between their needles. The resistance of the two films indicated thicknesses of 200 $\mu\mu$ and 110 $\mu\mu$ respectively. These numbers are evidently much too large, the error being due, as their experiments show, to a difference in the specific resistance of the film and that of the solution.

Again, the second black film will not appear when the films have been sealed in for any length of time, and the first black film may remain at a high thickness, particularly if the temperature is low and not increasing. In all cases, however, the limiting thickness of the first black film, before

* Lord Kelvin, 'Constitution of Matter,' p. 177.
† Phil. Trans. (A) 1893, p. 512.

breaking into the second, is about twice the thickness of the second. From this it might be inferred that the thickness of the second black film is possibly once the radius of molecular attraction, or some multiple, while the limiting thickness of the first is twice as great.

It is generally considered that the film whose thickness is once the radius of molecular attraction has a smaller tension than one twice as thick, and would thus be unstable. Maxwell*, however, has shown, on the assumption that the density is uniform in a region within the distance equal to the radius of molecular attraction from the surface of a liquid, and equal to the density of the liquid in mass, that a film whose thickness is once the radius of molecular attraction would have the same surface-tension as one twice as thick. That is, a film whose thickness is once the radius would be stable.

Statement of Results.—A curve illustrating the effect of temperature changes on the thickness of the sealed black film is first given.

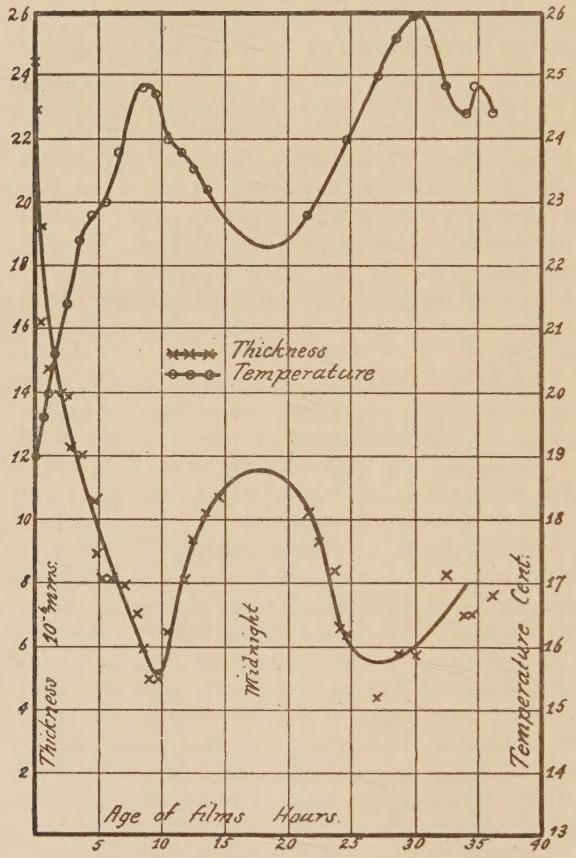
Fig. 4 (p. 508).—This curve was taken May 6th, with a 1 : 70 oleate of soda solution that had been sealed 24 hours. 38 of the original 54 films remained to the end of 40 hours. The abscissæ represent the age of the film in hours, and the ordinates, on the left, the mean thickness in $\mu\mu$; on the right the ordinates represent the temperature in degrees centigrade. No attempt was made to influence changes in the temperature. The whole apparatus was enclosed in a thick wooden box and the room carefully guarded against air-currents. No observation was made for the second black film as this was taken before its existence had been noticed. Apparently the inflexions of the thickness-curve follow, inversely, those of the temperature-curve, indicating an increase in thickness with a fall in temperature. Owing to the small deflexion and fewer films, the readings became more uncertain towards the end; hence, there the thickness-curve is not drawn as indicated by the points. When there are 54 films a deflexion of one fringe corresponds to a mean thickness of 16 $\mu\mu$.

Hygrometric Condition.—This curve, taken with the fact that exposure tends to thin the films, would indicate that the thickness depends on the hygrometric condition of the atmosphere about the films. An unsatisfactory attempt was made to measure the relative humidity with a wet and dry bulb hygrometer. Even with as great an exposure as was used in any observation, the difference in the readings of the thermometers was less than 0°·2, which at 23° C. would indicate a relative humidity greater than ·995.

* "Capillary Action," *Encyc. Brit.*

While the thickness of the first black film always diminishes with a rise in temperature, the thicknesses corresponding to any temperature are widely different for films from different

Fig. 4.



solutions similarly prepared, and even for different sets of films from the same solution. This is shown in the following tables, and may be partially due to irregularities in temperature and rate of thinning, but more probably to the difference in exposure and surface conditions of the solution.

The thinning of the sealed film because of a rise in temperature has an interesting bearing on a demonstration by Warburg*, that the thickness of a very thin film must

* Wied. *Ann.* vol. xxviii. (1886), p. 399.

diminish with an increase in the pressure of its surrounding saturated vapour. It was assumed, in accordance with Lord Kelvin's* surface-energy principle, that the thickness was so small that the surface-tension diminished with the thickness. As the pressure of the saturated vapour of a liquid increases with the temperature, it would be expected, from this principle, that the film would thin with an increase in the temperature. Whether the thinning is due to this cause or to a loss of water by evaporation from the surface of the films, such as Reinold and Rücker† have shown takes place at the surface of coloured films, seems to be an open question.

The remaining results are given in the following tables. The numbers in the first column indicate the age of the films in hours and minutes; the second, the number of films; the third, the mean thickness in $\mu\mu$; the fourth, the deflexion in fringes of sodium or white light; the fifth, the temperature inside of the casing; while the character of the films is given in the last column. The black film first formed is designated by b_1 and the next by b_2.

Table I.—This was taken September 9th with a 1 : 40 oleate of soda solution that had been sealed two hours. The films were all thinned to the b_2 films twice by warming a brass plate P (fig. 2), placed above the casing. From inspection of the table it may be seen that the thickness fell in 1 hour to 15 $\mu\mu$. So long as the temperature was 24°·6 it remained constant, and no b_2 films formed. The plate P was then gently warmed, and as a result the b_2 films formed suddenly on all the frames, while the mean thickness dropped to 6·3 $\mu\mu$. The plate was then removed, and the films all returned to the first black within 10 minutes. The operation was repeated two hours later with the same results. It may be observed that the mean thickness, just before all had begun to thin to b_2 and just as all had returned to b_1 films, was about 15 $\mu\mu$, while the thickness of the b_2 films was about 6·5 $\mu\mu$.

Table II.—This was taken September 15th, with a 1 : 70 solution of oleate of soda that had been sealed 24 hours. The deflexion began at slightly over two fringes, corresponding to a thickness of 33 $\mu\mu$, fell to 20 $\mu\mu$ in 3 hours, and to 15 $\mu\mu$ in 20 days. The room was left undisturbed for two weeks. The reading was then (412th hour), as usual, taken before the number of broken films was counted, and gave practically the same mean thickness. Two days later the brass plate was warmed, causing the first b_2 films to appear. The resulting

* Constitution of Matter, p. 179.
† Phil. Trans. vol. clxxii. (1881) p. 486.

thicknesses correspond closely to those in Table I. The limiting thickness of the b_1 films appears here as in Table I. to be about 12 $\mu\mu$.

Table III.—This was taken October 13th with a 1 : 70 oleate of soda solution to which 10 per cent. glycerine had been added. The casing had been sealed 24 hours. The most noteworthy feature is the great thickness and its slight increase at the beginning. This increase at the beginning has often been noticed with other solutions. The thickness fell to 28·6 $\mu\mu$ at the end of the 6th hour. The brass plate was then continuously heated for an hour while close to the casing, and the thickness fell to 11·5. No further thinning could be produced, even by heating the casing directly with the burner. The plate was then removed, and the temperature fell from 33°·4 C. to 25°, while the films came back to a mean thickness of 35 $\mu\mu$. Something similar to the b_2 films appeared on a few of the frames, but was never distinct as with the pure oleate solutions.

Table I.

1 : 40 Oleate of Soda Solution ; sealed 2 hours.

Age of Films.		Number of Films.	Thickness. 10^{-6} mms.	Fringes Deflexion.	Temperature. 0° Cent.	Character.
hours.	mins.					
...	...	52	...	...	25	b_1
...	2	51	27·6	1·6	24·6	,,
...	5	50	21·2	1·2	24·6	,,
...	15	49	18·0	1·0	24·6	,,
...	30	48	15·5	·85	24·6	,,
...	45	47	16·0	·85	...	,,
1	5	47	15·0	·80	24·6	,,
1	25	47	15·0	·80	...	,,
1	45	47	15·0	·80	24·6	,,
3	0	44	15·0	·75	24·6	,,
3	15	war	med			
3	15	44	13·1	·65	...	$4b_2$
3	16	42	6·3	·30	25·2	b_2
3	20	42	12·6	·60	25·2	$4b_2$
3	25	42	13·7	·65	...	b_1
4	5	42	13·7	·65	24·2	,,
4	25	42	13·7	·65	24·2	,,
4	45	42	15·8	·75	24·2	,,
5	5	41	16·0	·75	...	,,
5	5	w	med			,,
5	7	41	6·5	·30	25·2	b_2
5	45	36	12·3	·50	24·8	b_1

TABLE II.—1 : 70 Oleate of Soda Solution ; sealed 24 hours.

Age of Films.		Number of Films.	Thickness. 10^{-6} mms.	Fringes Deflexion.	Temperature. 0° Cent.	Character.
hours.	mins.					
...	...	53	33·4	2·00	22·4	b_1
3	...	53	20·0	1·20	21·8	,,
16	...	53	18·4	1·10	21·0	,,
40	...	53	18·4	1·10	21·0	,,
68	...	52	17·0	1·00	21·4	,,
92	...	51	15·7	·90	21·0	,,
111	...	51	15·7	·90	20·4	,,
412	...	37	15·5	·65	22·0	,,
435	...	37	15·5	·65	21·6	,,
455	...	37	15·5	·65	21·0	,,
455	...	war	med	...	...	,,
455	3	37	14·3	·60	22·2	,,
...	6	37	12·0	·50	22·8	$7b_2$
...	7	war	med	...	...	$3b_1$
...	8	37	6·7	·28	22·8	b_2
...	9	37	6·0	·25	23·0	,,
...	16	36	6·1	·25	23·1	,,
...	24	36	7·3	·30	22·8	
...	40	36	8·6	·35	22·6	
456	5	35	8·8 12·6	·35 ·50	22	
...	25	35	12·6	·50	21	$4b_2$
457	25	31	14·2	·50	21	b_1

TABLE III.—1 : 70 Oleate of Soda Solution to which 10 per cent. glycerine was added ; sealed 24 hours.

Age of Films.		Number of Films.	Thickness. 10^{-6} mms.	Fringes Deflexion.	Temperature. 0° Cent.	Character.
hours.	mins.					
...	...	53	...	...	18·0	b_1
...	2	53	38·4	2·3	18·0	,,
...	10	53	40·0	2·4	18·5	,,
...	20	53	41·7	2·5	18·5	,,
...	55	52	39·0	2·3	19·0	,,
1	40	52	38·2	2·25	20·5	,,
3	40	52	34·0	2·00	22·0	,,
5	40	51	31·2	1·80	22·6	,,
7	...	51	28·6	1·65	23·8	,,
	war	med	...	...	...	,,
...	5	51	26·0	1·50	24·7	,,
...	9	51	22·5	1·30	25·3	,,
...	14	51	17·3	1·00	26·4	,,
...	25	51	13·4	·85	28·4	,,
...	34	51	12·8	·75	31·0	,,
...	40	50	11·5	·65	32·0	,,
...	55	50	11·5	·65	33·4	,,
8	war	med	...	...	...	,,
...	...	46	14·4	·75	32·0	,,
...	25	38	31·4	1·35	26·4	,,
10	20	30	35·2	1·20	25·0	,,

TABLE IV.—1:70 Oleate of Soda Solution.

Age of Films. hours.	Age of Films. mins.	Number of Films.	Thickness 10^{-6} mms.	Fringes Deflexion.	Temperature, 0° Cent.	Character.
Obs. I.—Freely exposed.						
...	...	52	10·2	·60	25·8	...
...	3	49	6·35	·35	25·8	b_2
...	7	48	6·45	·35	...	,,
Obs. II.—Sealed partially, 3 hours.						
...	...	53	16·7	1·00	25·2	b_1
...	10	52	11·9	·70	25·3	,,
...	55	51	6·1	·35	26·2	b_2
1	15	51	8·7	·50	25·8	$16\,b_1$
2	...	51	10·4	·60	23·6	$20\,b_1$
Obs. III.—Freely exposed at ends.						
...	...	53	16·7	1·00	24·3	b_1
...	2	53	10·8	·65	24·6	$16\,b_2$
...	37	52	5·9	·35	26·0	b_2
1	17	41	6·5	·30	26·6	,,
Obs. IV.—Sealed firmly, 10 minutes.						
...	...	53	16·7	1·00	24·0	b_1
...	35	53	11·7	·70	24·4	$2\,b_2$
4	20	51	7·0	·40	25·6	$46\,b_2$
4	25	war	med	...	...	.....
4	25	45	5·9	·30	28·0	b_2
4	32	41	6·5	·30	31·0	,,
Obs. V.—Sealed firmly, 2 days.						
...	...	53	30·0	1·8	23·0	b_1
...	5	53	21·7	1·3	23·0	,,
1	5	53	15·0	·9	24·2	,,
3	30	53	15·0	·9	25·1	,,
Obs. VI.—Sealed firmly, 4 days; low temp.						
...	...	53	30·0	1·80	18·0	b_1
3	...	52	17·0	1·0	19·3	,,
8	...	51	13·9	·8	21·0	,,
24	...	48	14·7	·8	19·8	,,
Obs. VII.—Sealed 5 days; high temp.						
...	...	53	15·0	·90	29·8	b_1
...	2	53	10·0	·60	30·0	$10\,b_2$
...	10	53	8·3	·50	30·2	$20\,b_2$
2	15	48	12·0	·65	30·0	b_1
6	15	40	15·5	·70	28·4	,,

TABLE IV. (*continued*).

Age of Films. hours.	Age of Films. mins.	Number of Films.	Thickness 10^{-6} mms.	Fringes Deflexion.	Temperature. 0° Cent.	Character.
Obs. VIII.—Sealed 6 days; falling. temp.						
...	...	53	33·4	2·00	18·2	b_1
1	...	53	19·2	1·15	17·5	„
6	...	53	18·4	1·10	17·5	„
Obs. IX.—One side unsealed, 16 hours.						
...	...	53	21·7	1·30	17·2	b_1
...	5	52	13·6	·80	17·2	$4\,b_2$
...	8	51	11·3	·65	17·2	$6\,b_2$
...	28	42	8·4	·40	17·2	$20\,b_2$
1	...	34	7·7	·30	17·4	
1	4	33	6·7	·25	17·6	b_2
Obs. X.—Exposed; 20 per cent. glycerine.						
...	...	52	29·0	1·70	22·2	b_1
...	10	52	22·0	1·30	22·8	„
1	50	52	22·0	1·30	23·5	„
5	0	49	23·5	1·30	23·5	„

Table IV.—This was taken Oct. 18th and the ten days following on a 1:70 oleate-of-soda solution. The solution was then drawn out and 20 per cent. glycerine boiled with it. Only part of a few of the observations are given, the object being to illustrate the effect of exposure and change of temperature on the thickness of the films.

Observation I.—These readings were taken soon after the solution was prepared, and as soon as it had cooled down to the temperature of the room. The films were freely exposed. Within three minutes the b_2 films had formed on all of the frames.

Observation II.—At the end of Obs. I. the casing was partially sealed and II. taken three hours later. The mean thickness was greater and did not fall so rapidly, though the same might have been the case (judging from other observations) had there been no sealing.

Observation III.—This was taken Oct. 19th, 24 hours later, with the same sealing, and shows about the same thicknesses as in II.

Observation IV.—This was taken Oct 20th, the solution having been firmly sealed 10 minutes when the frames were raised. The second reading gives 11·7 as the limiting thicknesses of the b_1 films. At the end of four hours not all had

become b_2 films, which shows the effect of sealing on the character of the films. But on slightly warming the casing all suddenly became b_2 films at a thickness of 6 $\mu\mu$.

Observation V.—This was taken Oct. 22nd, with the same sealing as in IV. The greater thickness is evidently due to the atmosphere of the films having been sealed for two days.

Observation VI.—This was taken Oct. 24th, two days later, with the same sealing, but at a temperature several degrees lower, and gives practically the same thicknesses.

Observation VII.—This was taken Oct. 25th at a temperature about 10° higher. The fall in thickness may have been partially due to a leaking-in of the air. However, this is a fair example of all observations on pure oleate solutions at high temperature.

Observation VIII.—This was taken Oct. 27th, with a low and falling temperature, and shows a great thickness for over six hours. The thicknesses are about the same as in VI.

Observation IX.—This was taken Oct. 28th after one side of the casing had been unsealed for 16 hours. The fall in thickness even at this low temperature corresponds closely with that of Obs. II., at a higher temperature, taken ten days previously under similar conditions. All the films broke readily into the b_2 films as soon as the lights L and S (fig. 1) were left burning.

Observation X.—This was taken some time later after 20 per cent. glycerine had been added to the solution, and even with the most exposed atmosphere shows a great thickness. No b_2 films appeared. The casing was then sealed, but the solution had become so contaminated that the films broke too readily to permit of any trustworthy readings being made.

Solutions of Different Compositions.—No difference could be observed between the pure oleate-of-soda and oleate-of-potash solutions. The second black film formed under the same conditions, and with the same characteristics, with both solutions. However, with the addition of either glycerine or potassium nitrate the character of the black film was completely changed. When freely exposed or heated, both would show slowly moving eddies of darker regions. When potassium nitrate was added these eddies broke up into tiny flecks moving rapidly about in the film; but never formed in clusters on the frames, as was the case with the pure oleate solutions. While the effect of the glycerine was to increase the thickness of the black film, that of the potassium nitrate was to diminish the range. With an oleate-of-soda solution to which 5 per cent. potassium nitrate had been added, the maximum mean thick-

ness observed was 13·8 $\mu\mu$, while for the most freely exposed the minimum was 7·5 $\mu\mu$.

Effect of an Atmosphere of Carbon Dioxide.—The effect of introducing an atmosphere of carbon dioxide while the black films were formed was remarkable. The films all suddenly became coloured, and did not again thin to the black film. A thick white precipitate formed on the solution at the bottom of the films and gradually covered the surface. A similar precipitate was often noticed at the bottom of the films, even when the case had been sealed, thus indicating that possibly the atmosphere of the films always contained carbon dioxide.

Conclusions drawn from Results of the First Method.

Considering the observations here given and many others that were made, these conclusions are:—

(1) That the thickness of the black film is independent of the proportions of oleate and water. The truth of this may be seen in comparing the readings in Table I., taken with a 1:40 solution, with those of Tables II. and IV., taken with a 1:70 solution. The same is borne out by many other observations on pure oleate solutions varying in proportion from 1:40 to 1:100.

(2) That the thickness of the black film with a sealed atmosphere diminishes as the temperature rises. This is illustrated in the curve of fig. 4 (p. 508) most clearly. But it is also shown to be true for sudden changes in temperature in the warming process of all the tables.

(3) That the thickness of the exposed black film is ultimately that of the second black, which is constant and independent of the temperature. This is shown by comparison of observations I., II., III., and IX. of Table IV. A number of observations indicated that the thickness of the second black film was not constant. However, as the greatest difference in the deflexion corresponding to a certain number of films was never more than a tenth of a fringe, it is difficult to say whether this corresponds to a real difference in the thickness of the second black film or not.

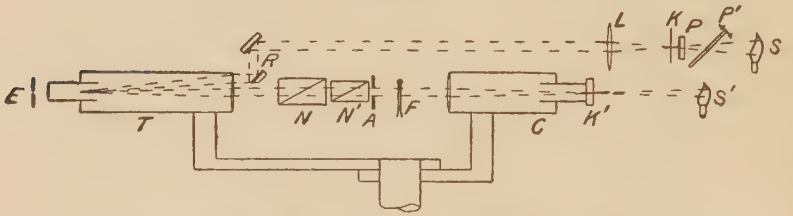
Method II.

The idea of determining the thickness of the black film by measuring the intensity of the light reflected at different angles of incidence was suggested by Prof. Michelson. The measurements were made by comparing the images of two slits at the focus of the telescope of a spectrometer. The light from the slit of the collimator entered the telescope after

reflexion from the film. The other slit was that of a silvered-glass photometer.

Description of the Apparatus.—The photometer consisted of a piece of plate-glass P (fig. 5), lightly silvered on one side with a wedge-shaped silver film and placed behind the

Fig. 5.



slit K. The sensitiveness was increased by placing at P′ a sheet of ground glass which was capable of rotation about a horizontal axis. A lens, L, rendered the rays from S parallel, after which they were reflected through a portion of the objective of the telescope by means of a pair of mirrors, R. Two nicols, N and N′, were placed in front of the objective, through which all light reaching the telescope from the collimator passed. A small circular aperture, A, was placed in front of the nicols so as to allow the light to pass through their central portions only. Precautions were taken in observations at all angles of incidence to have the reflected wave-front completely cover this aperture. Another smaller aperture, E, helped in properly placing the eye.

Method of Observation.—The manner of making an observation was as follows:—Set the two nicols parallel; turn the collimator to the angle of incidence at which the reading is wanted; raise the film, F, and turn it until the image of the collimator-slit is close beside that of the photometer. Then, as soon as the black film is formed, adjust the photometer so that both images have the same intensity. The film is then removed, the collimator turned into line with the telescope, and the nicol N turned about its axis until the photometer is again matched.

Theory of the Method.—The intensity of the reflected light is given by the equation

$$I = \cos^2\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where θ is the angle through which the nicol N is turned and I is one half of the light incident on the front nicol N′ (neglecting loss due to reflexion). By properly setting the front nicol, the observation may be made with light polarized

in a plane at any angle with the plane of incidence. The error due to an incorrect setting will be a minimum when the light is polarized either in or perpendicular to the plane of incidence.

Airy's formula * expressing the relation between the intensity of the reflected light and the thickness of the film is

$$I = \frac{4b^2 \sin^2 \frac{\delta}{2}}{(1-b^2)^2 + 4b^2 \sin^2 \frac{\delta}{2}}, \quad \ldots \quad (2)$$

where b is the coefficient of reflexion,

$$\delta = \frac{4\pi\mu D \cos r}{\lambda},$$

μ the index of refraction in the film, and D the thickness of the film.

Putting

$$A = \frac{\lambda}{2\pi\mu \cos r},$$

$$B = \frac{1-b^2}{2b};$$

and solving the equation for D,

$$D = A \sin^{-1} B\sqrt{\frac{I}{1-I}}$$

$$= A \sin^{-1} BI^{\frac{1}{2}} = ABI^{\frac{1}{2}}, \text{ approximately}$$

(since

$$D = ABI^{\frac{1}{2}}\{1 + \tfrac{1}{2} \cdot \tfrac{1}{3} B^2 I + \ldots\}$$

and

$$B^2 I < \cdot 008),$$

since in nearly all cases coming into consideration

$$I < \cdot 004.$$

Therefore from (1)

$$D = AB \cos \theta.$$

Since θ is nearly $\frac{\pi}{2}$, it is evident that the thickness D is approximately proportional to the complement of θ.

Method of representing the Results.—Instead of computing

* Undulatory Theory of Optics, p. 53.

the thickness for each observation, the intensity-curves were plotted for a series of curves for different thicknesses of film, but alike in other respects. The observed intensities were then plotted on the same plate. The broken lines on figs. 6 and 7 represent the calculated intensity-curves for light polarized respectively in and perpendicular to the plane of incidence. The constants used in formula (2) for the calculations were

$$\mu = 1{\cdot}333,$$

$$\lambda = 550\,\mu\mu.$$

The intensity-curves for D equal to 5, 6, 7, 8, 9, and 12 $\mu\mu$ are plotted in fig. 6, and 5, 7, and 9 in fig. 7, for angles of incidence varying from 0° to 70°. The abscissæ represent the angles of incidence, while the ordinates represent the fractional part of the light incident on the second nicol N (with the collimator in the zero position), that is reflected from the film.

Statement of Results.—The results of some observations at an angle of incidence of 45° are first given in Tables V. and VI. Two gas-jets were used as sources in Table V., while in all other observations by this method the two sources, S and S′ (fig. 4), were two Welsbach burners. The number of the observation is given in the first column and the intensity in the second, calculated from the values of θ in the third. In the last column the thickness is given both in terms of the wave-length and in absolute measure, the wave-length being assumed to be 550 $\mu\mu$.

Table V.

Polarized at 45° to plane of incidence; angle of incidence 45°.

Obs.	Intensity.	$\theta - \frac{\pi}{2}$.	D.	
I.	·00106	1°·86	$\frac{\lambda}{73}$	10^{-6} mms. 7·5
II.	·00073	1·57	$\frac{\lambda}{88}$	6·2
III.	·00098	1·80	$\frac{\lambda}{77}$	7·1
IV.	·00075	1·56	$\frac{\lambda}{88}$	6·2
			Mean	6·7 $\mu\mu$

TABLE VI.

Polarized in plane of incidence; angle of incidence 45°.

Obs.	Intensity.	$\theta - \frac{\pi}{2}$.	D.	
				10^{-6} mms.
I.	·00193	2·53	$\frac{\lambda}{77}$	7·1
II.	·00187	2·49	$\frac{\lambda}{75}$	7·3
III.	·00247	2·86	$\frac{\lambda}{69}$	8·0
IV.	·00225	2·74	$\frac{\lambda}{72}$	7·6
V.	·00168	2·35	$\frac{\lambda}{85}$	6·5
VI.	·00239	2·39	$\frac{\lambda}{83}$	6·6
			Mean	7·2 $\mu\mu$

Table V.—In this table the plane of polarization made an angle of 45° with the plane of incidence. The first two observations were made April 22nd on a 1: 70 oleate-of-soda solution that had stood in the vessel on the table of the spectrometer exposed to the air of the room several days. The last two were taken with a newly prepared solution. The mean thickness is about 7 $\mu\mu$.

Table VI.—This was taken with a similar solution, but with the plane of polarization in the plane of incidence. The mean thickness is about 7 $\mu\mu$.

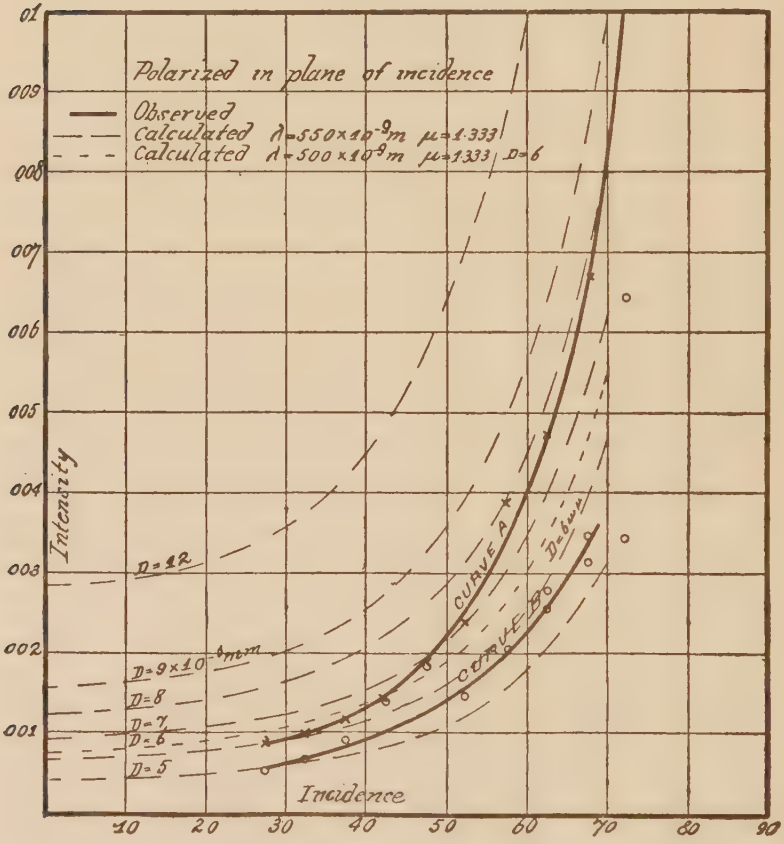
Continuous readings were then made with a 1: 70 oleate-of-soda solution at different angles of incidence. The results are plotted in curves A, B, and C of figs. 6 and 7. Each observation of the intensity plotted is calculated from the mean of ten readings, taken alternately, on opposite sides of the crossed positions of the nicols. A separate film was used for each point. Readings were taken at intervals of 5°, with angles of incidence varying from 22°·5 to 72°·5.

Curve A (p. 520).—This was taken May 11th with a solution that had stood one night exposed to the atmosphere of the room. The intensity of the reflected light corresponds to that from a film whose thickness is about 7 $\mu\mu$. The apparent increase in the thickness at high angles of incidence may have been due to the difficulty in matching the more intense images. The temperature of the room was about 25° C.

Curve B.—This was taken July 12th with a newly prepared solution. Between these readings and those in A the

apparatus had been taken down and entirely readjusted. This may possibly account for the difference in the readings, although it may also have been due to a difference in the solutions. Some of the points lie above a smooth curve through the others, which may be due to imperfect films, as some difficulty was experienced in getting stable films. The thickness of the films is about 6 $\mu\mu$. The temperature of the room was about 23° C.

Fig. 6.

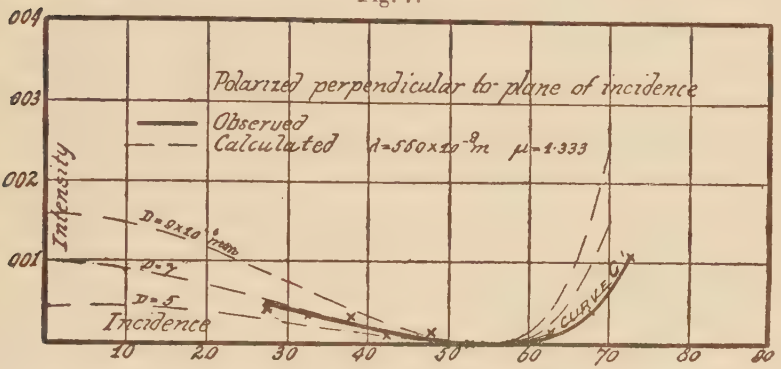


Curve C.—This was taken July 13th, with the same solution as B, that had stood exposed one night. The plane of polarization was perpendicular to the plane of incidence. The intensity fell until the angle of incidence was 52°·5, at which the image of the collimator-slit could barely be

distinguished. After this for quite an interval no image could be seen. At 57°·5 the image was very distinct. The rise in the intensity was remarkably rapid beyond the polarizing-angle.

The effect of using different values for the mean wave-length in the computed curves is illustrated in fig. 6 by the dotted

Fig. 7.



line, which is the computed intensity-curve for D equal to 6 $\mu\mu$ on the assumption that λ is 500 $\mu\mu$.

Comparison of the two Methods.—The first method offers many advantages over the second. The films could be seen, the temperature of their atmosphere measured, and its hygrometric condition more easily controlled in the first method. But it was not possible to have the films thin at the same rate; hence the readings represent only mean thicknesses. In many cases there was, no doubt, a wide difference in thickness, at any elevation, on different films, and even on the same film.

The film in the second method was 2 cms. by 9 cms., and was exposed at two openings each about a square centimetre in area, and would thus be an "exposed" film.

Probably the most striking feature in the comparison of the results of the two methods is the nearness of the thickness obtained in the second method to that in the first with an exposed film.

It may be remarked that the results of the second method were all obtained before the second black films had been noticed. Although it was impossible to see the second black film in the second method, there can be no doubt but that the first black broke immediately into the second; for such was the case in the first method even when the exposure was ever so much less.

Although the results of the second method correspond to what should be expected from the first, they should probably not be considered to prove more than that the ordinary laws of reflexion hold at the surfaces of such thin films.

Conclusions.—The conclusions to be drawn from the work, briefly stated, are:—

(1) That the thickness of the black film of a soap-solution is not constant, and may vary from 6 $\mu\mu$ to 40 $\mu\mu$.

(2) That the film of a pure oleate solution may consist of two black films, the thickness of the second being about half the limiting thickness of the first, which is about 12 $\mu\mu$.

(3) That the addition of glycerine or potassium nitrate to a pure oleate solution prevents the appearance of the second black film. While in the first case the thickness is greater, in the second the range of the thickness is smaller.

The observations by the first method have been repeated by Mr. Chamberlain; the mean of his results for the thickness of the second black film was 6·2 $\mu\mu$, and for the limiting thickness of the first black film 11·2 $\mu\mu$.

It is here desired to acknowledge indebtedness for many ideas in both methods to Prof. Michelson; and also to thank him for his interest and encouragement in the work, as well as for giving us an instrument so beautifully adapted to work of this character. Many suggestions should also be acknowledged to Associate Prof. Stratton, particularly in regard to the apparatus used. Finally, it is desired to thank Dr. Millikan for suggestions in the preparation of the manuscript.

Ryerson Physical Laboratory,
University of Chicago, March 1st, 1899.